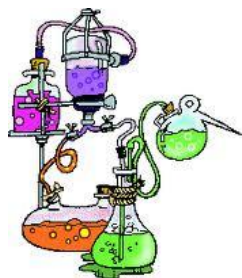


Supramolecular Chemistry for Pressure Sensitive Adhesives ?

Gordon Seminar 2014

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Sandrine Pensec, Laurent Bouteiller
LCP, UPMC, Paris, France

PSA = Pressure Sensitive Adhesives

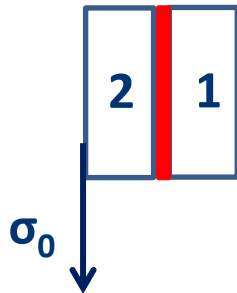


A material which sticks on almost any surface by simple contact, without chemical reaction



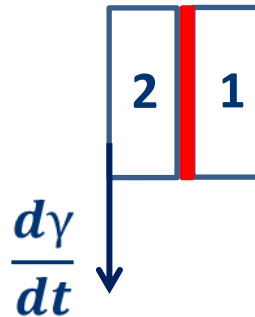
Solid

Non flowing



Liquid

Dissipative



Viscoelastic Materials

PSA = Pressure Sensitive Adhesives



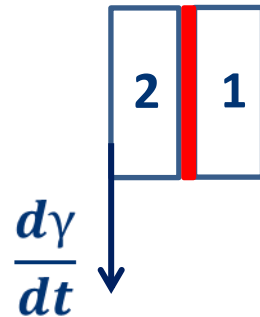
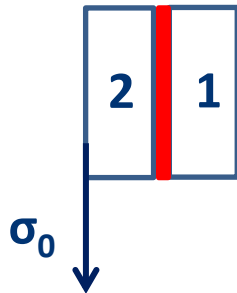
A material which sticks on almost any surface by simple contact, without chemical reaction



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Viscoelastic Materials

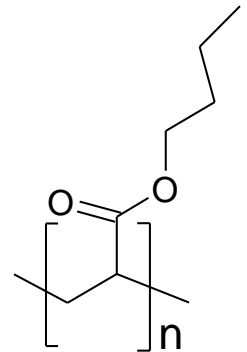
*Classic Formulation
(Acrylic)*

Low $T_g < -40^\circ\text{C}$

For ex, PnBA $\approx -50^\circ\text{C}$

Long entangled polymers Chains

Light cross-linking + Pendant Short Chains



Challenge of our project :

Is it possible to get a viscoelastic behavior required for a PSA with **unentangled molecules** with **strong** but **reversible** interactions ?



New Chemical Parameters

High Solubility in Organic Solvent

What is required ?

Strongly interacting moieties separated by flexible polymer chains.



Supramolecular System

Challenge of our project :

Is it possible to get a viscoelastic behavior required for a PSA with **unentangled molecules** with **strong** but **reversible** interactions ?



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High Solubility in Organic Solvent

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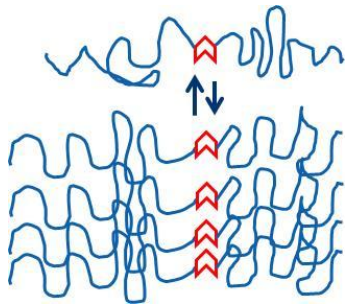
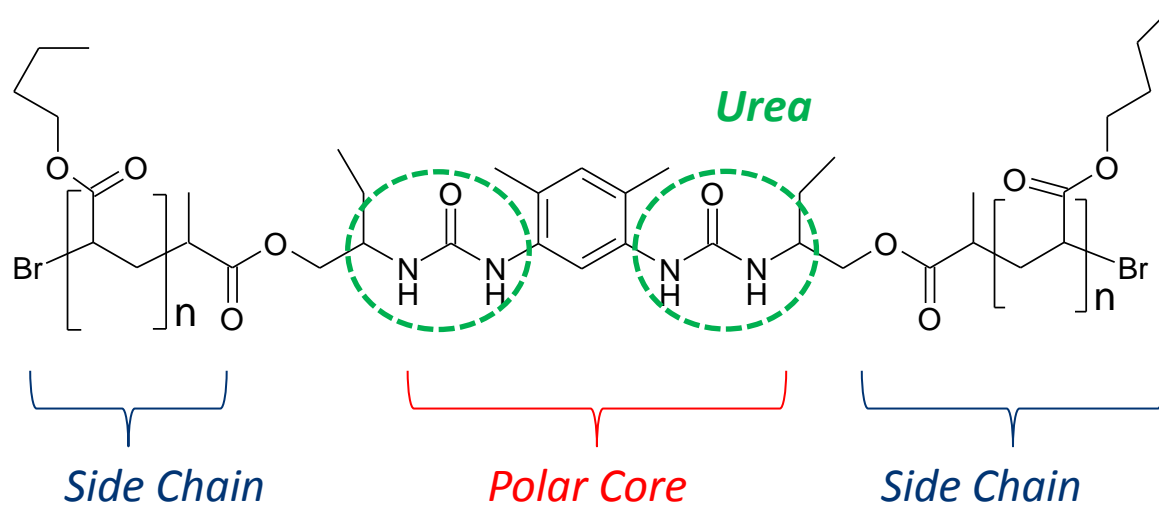
Supramolecular System

Strategy

- Synthesize Supramolecular **Model Systems** with a highly controlled chemical structure.
- Systematic **Rheological** and **Adhesive** Characterization

Model System n°1

Bis-urea Xylene Center-Functionalized PnBA



Self-assembly
of Stickers¹

¹Pensec et al, *Macromolecules*, 2010, 43, 2529-2534

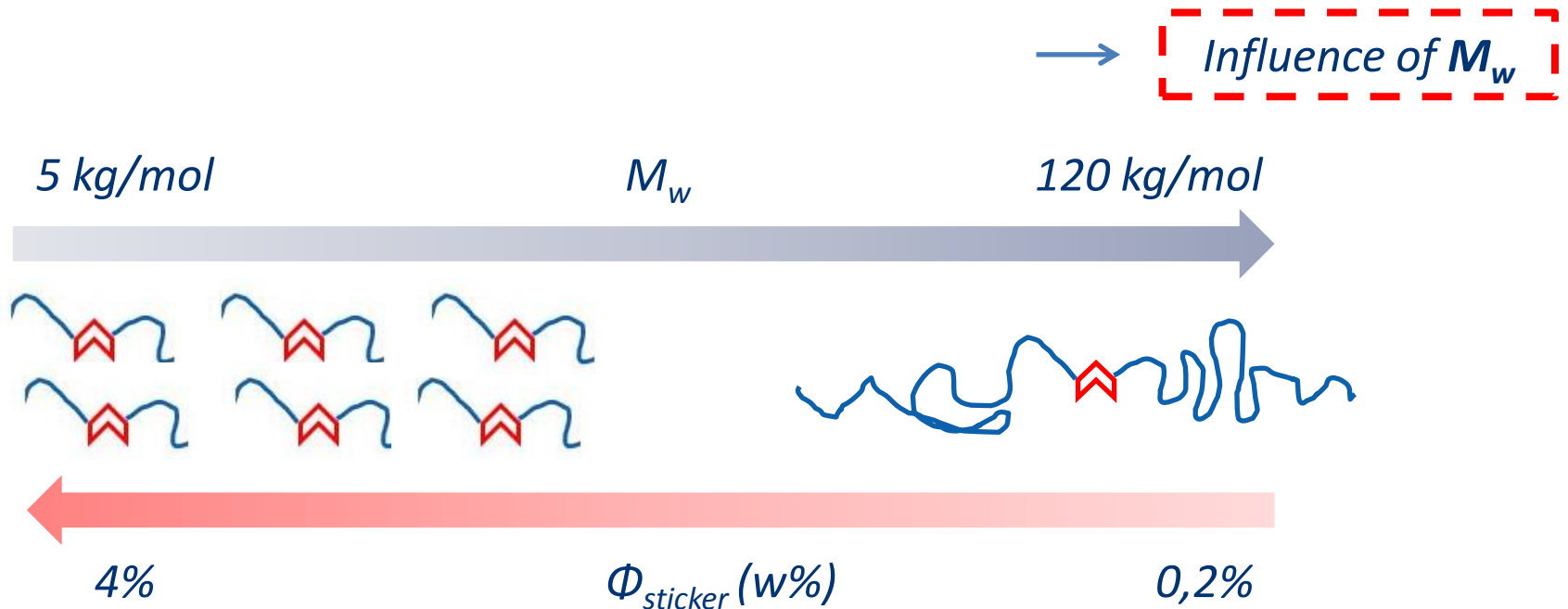
¹Courtois et al, *J. Adv. Funct. Mater*, 2010, 20, 1803-1811

Strategy for Synthesis

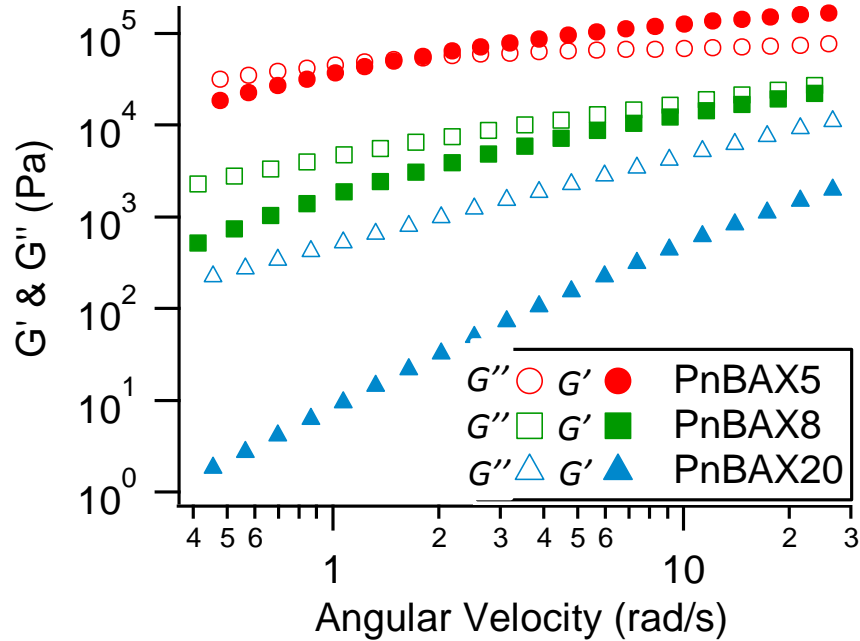
Sticker is the **initiator** of the polymerization.



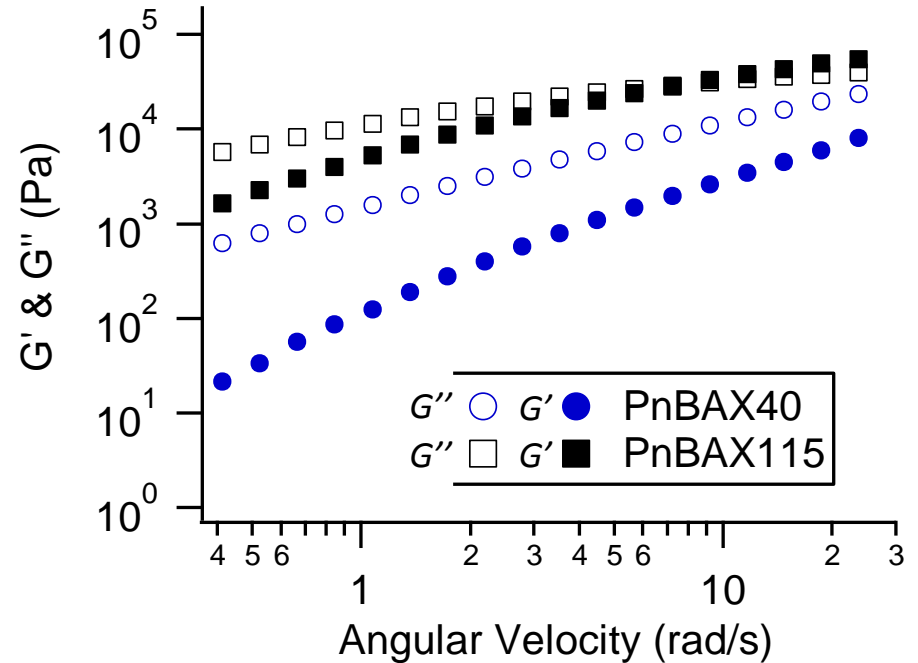
Growth of two symmetric side chains by ATRP ($I_p < 1,4$).



Viscoelastic behavior at 25°C (in the melt state)



At a fixed ω , G' & $G'' \searrow$ if $M_w \nearrow$



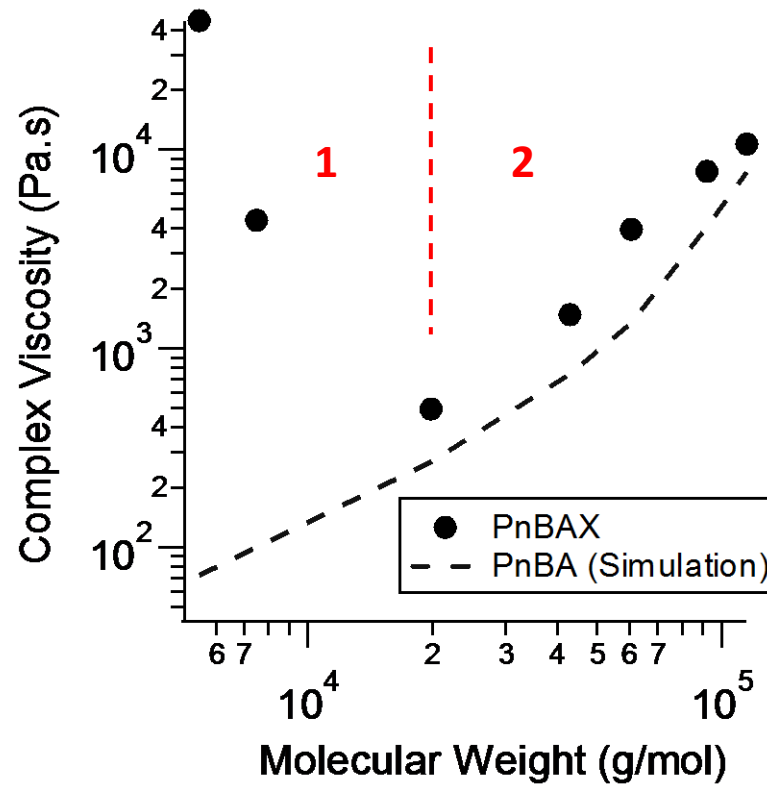
At a fixed ω , G' & $G'' \nearrow$ if $M_w \nearrow$

All Viscoelastic Fluids at RT

Viscoelastic behavior at 25°C (in the melt state)

$$\eta^* = \sqrt{(G'{}^2 + G''{}^2)} / \omega$$

$$\eta^*(1 \text{ rad/s}, 25 \text{ C})$$



⇒ **Two regimes**

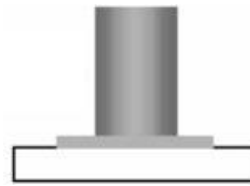
- $\tau \approx f(\phi_{\text{sticker}})t$ for $M_w \leq 20\text{kg/mol}$
- $\tau \approx f(L_{\text{PnBA}})$ for $M_w \geq 20\text{kg/mol}$

Adhesion of thin acrylic films

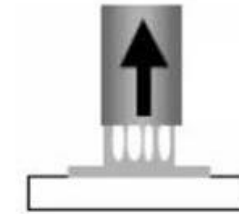
Probe-tack Experiments – Flat Punch

Steel probe ($\Phi \approx 1\text{cm}$)

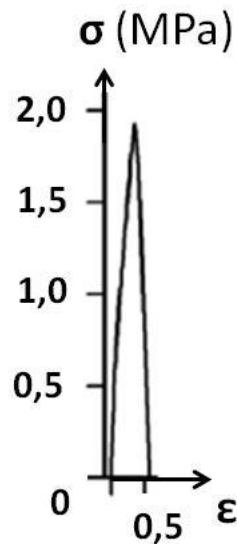
Thin Film ($h \approx 100\mu\text{m}$)



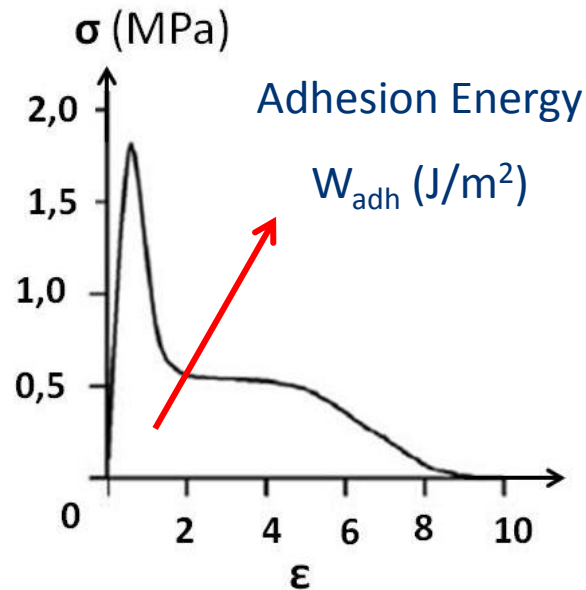
Contact ($t \approx 10\text{s}$)



Debonding ($V = 100\mu\text{m/s}$)



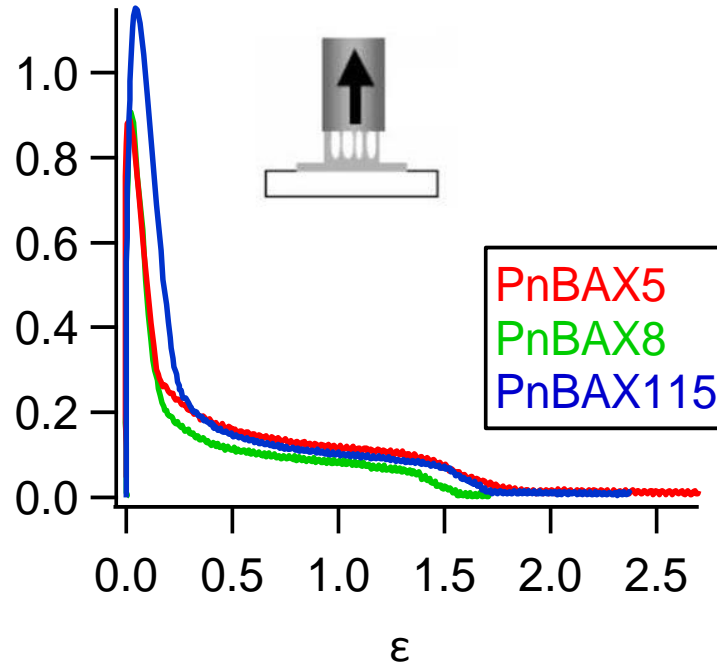
Elastic



Viscoelastic / Viscous

Adhesion test

σ (MPa) *Probe-tack test (100 μ m/s) Steel Probe*

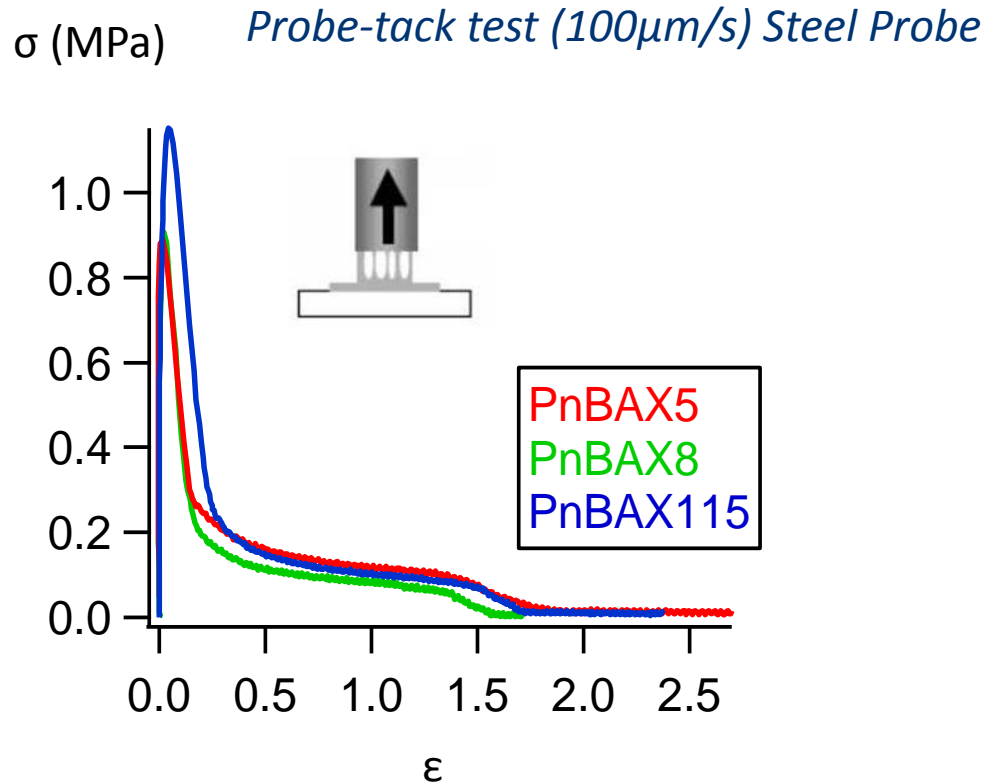


$W_{adh} \approx 30-50 \text{ J/m}^2$



$W_{adh} \ll W_{adh} \text{ (PSA)} \approx 100 \text{ J/m}^2$

Adhesion test



$$W_{adh} \approx 30-50 \text{ J/m}^2$$



$$W_{adh} \ll W_{adh} \text{ (PSA)} \approx 100 \text{ J/m}^2$$

How to strengthen
our supramolecular system ?

Entangled Chains

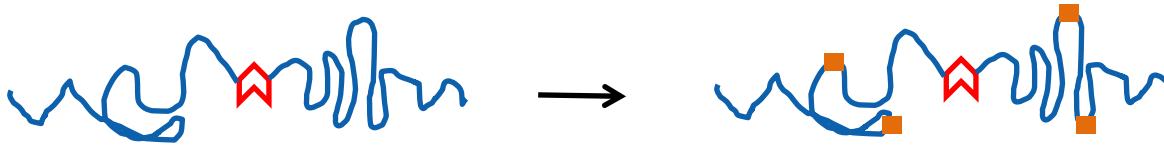
+

A high Density of Sticker

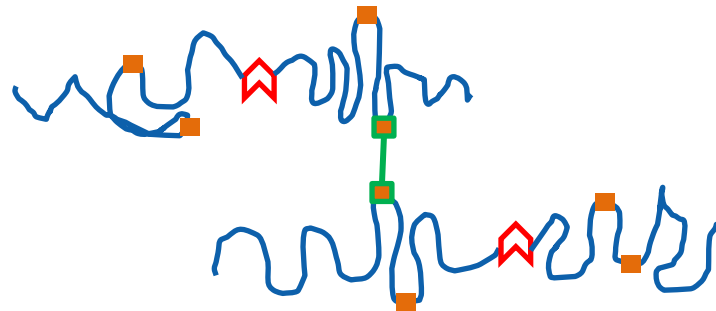
Supramolecular Copolymers & Resins

Entangled Chains with several stickers per chain

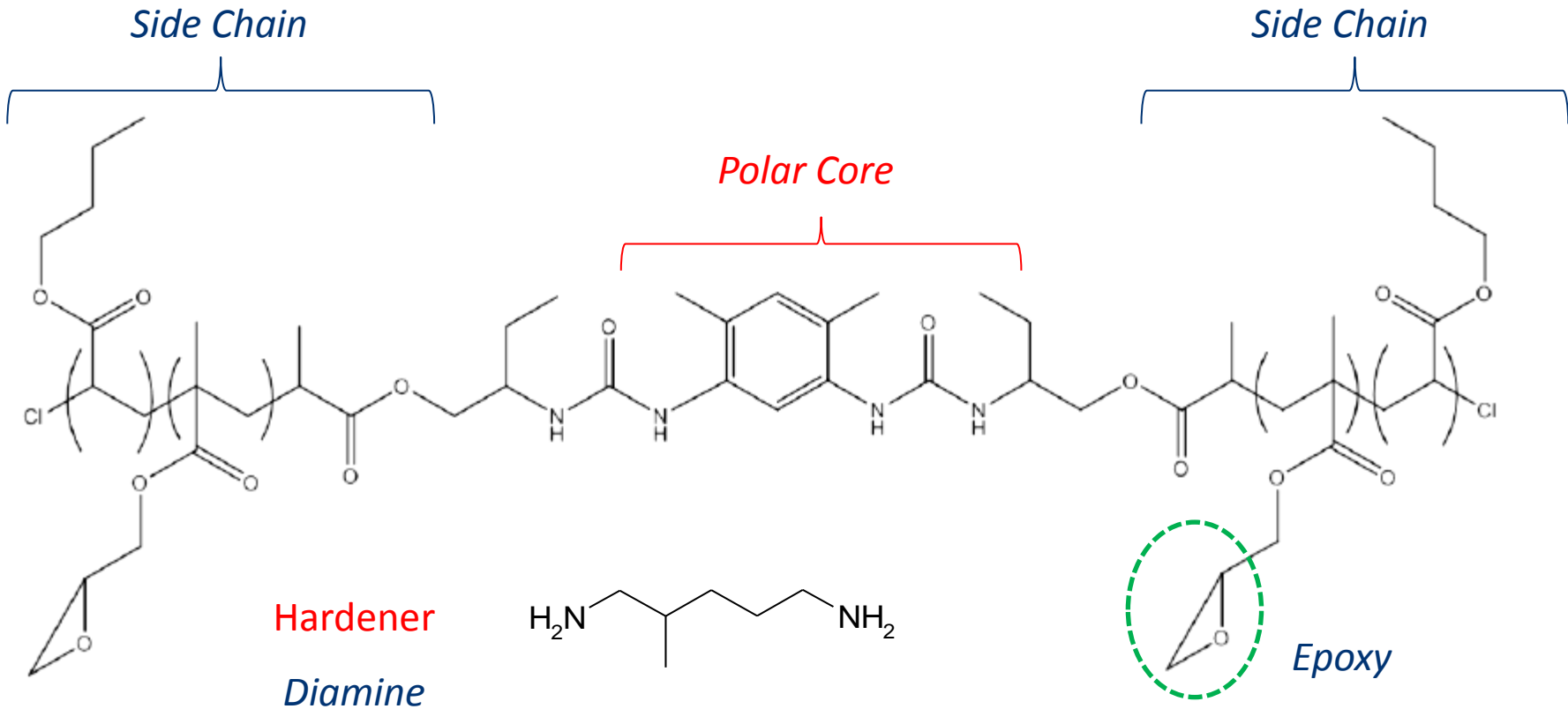
→ Incorporate reactive monomers in the side chains of our PnBAX



→ Cross-link partially with cross-linker (or hardener)



Supramolecular Copolymers & Resins



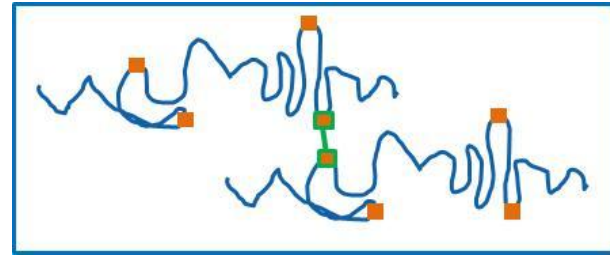
Chemical Parameters for
the copolymer structure

→ $M_w \approx 10\text{kg/mol}$
8 GMA per polymer chain

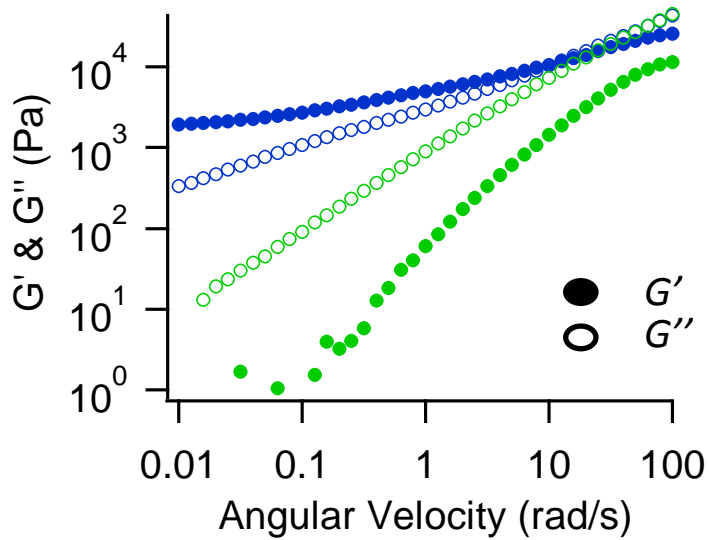
Copolymer **without** Xylene Core



Uncross-linked Copolymer

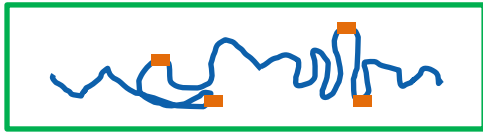


Lightly Cross-linked Copolymer
w%(hardener) = 0,8%

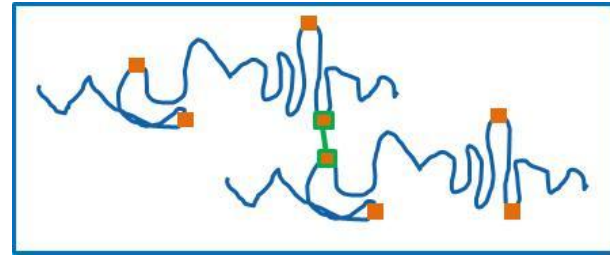


Frequency Dependence for G' & G'' at 25°C

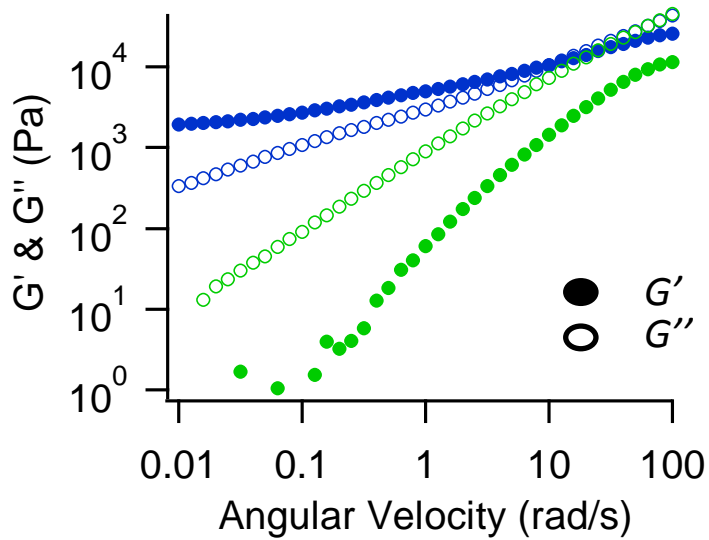
Copolymer **without** Xylene Core



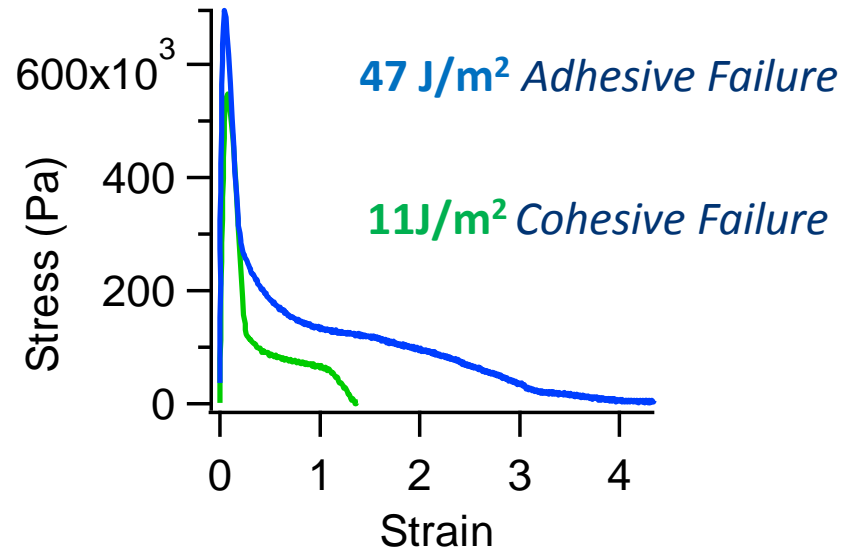
Uncross-linked Copolymer



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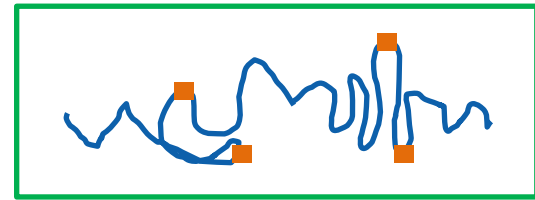
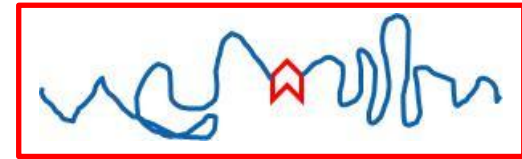
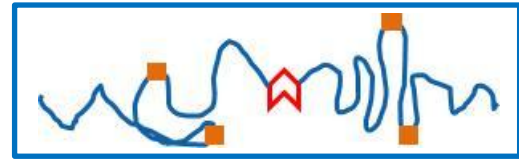
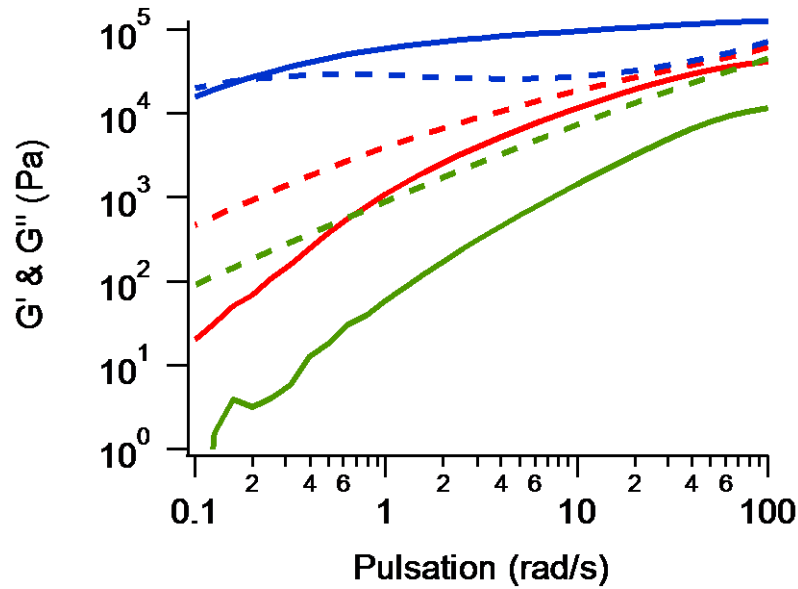
Frequency Dependence for G' & G'' at 25°C



Strengthening our PnBA Matrix by Chemical Cross-linking



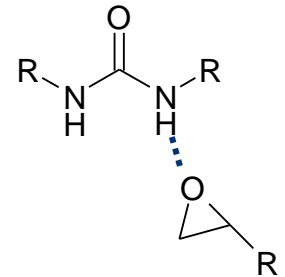
Copolymer **with** Xylene Core



High Viscoelastic Moduli

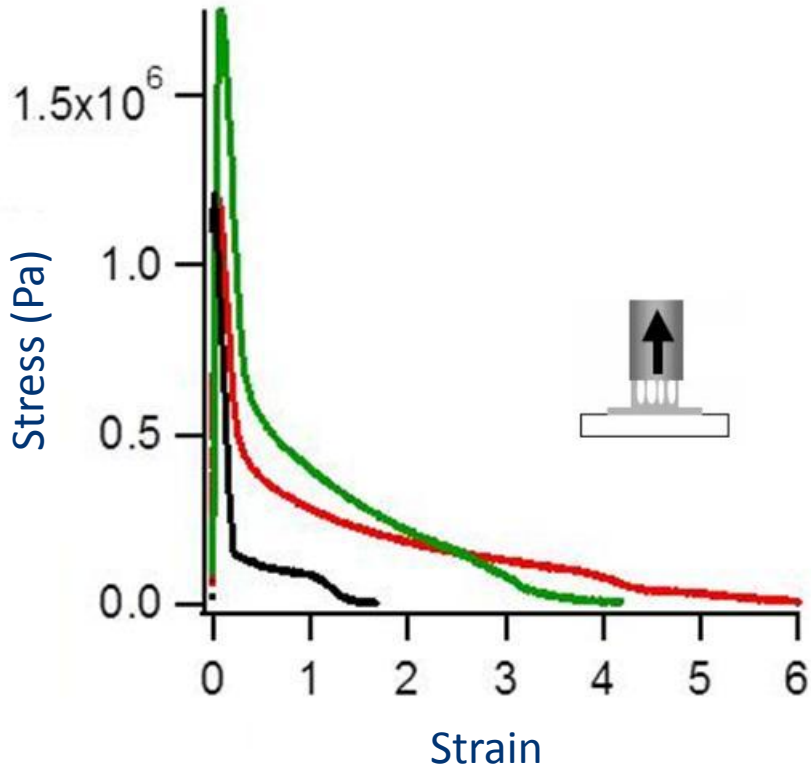


Strong Interactions between
Epoxy / Xylene



Strengthening our PnBA Matrix by Epoxy / Urea Interaction

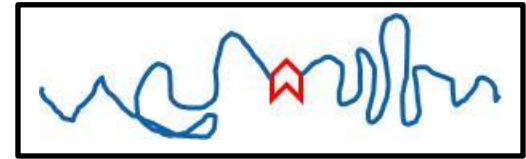
Copolymer **with sticker**



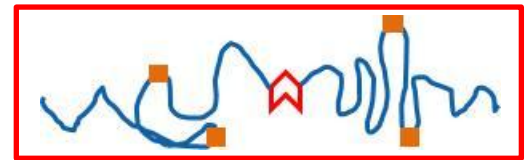
Probe-tack 100 μ m/s – Steel Probe



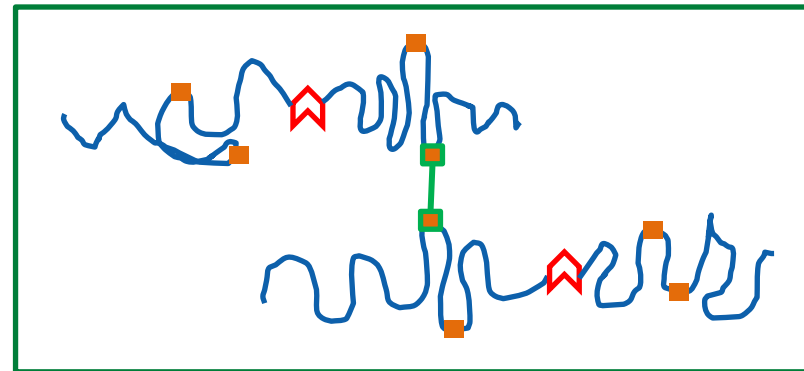
High Improvement of Adhesive Properties



35 J/m² Cohesive Debonding



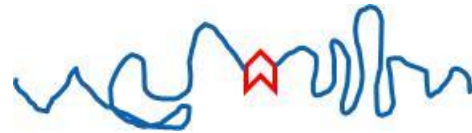
104 J/m² Cohesive Debonding



0,04% 104 J/m² Adhesive Debonding

Conclusion

Center-functionalized PnBA

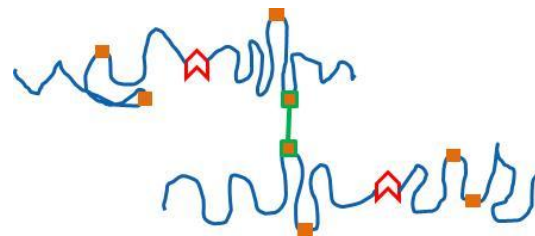


Viscoelastic Fluids



Center-functionalized Pn(BA-GMA) lightly Cross-linked

Soft Dissipative Solid



Supramolecular Interactions + Chemical Cross-linking

Promising Adhesion